Geochemistry Downstream from Steel Slag Leach Beds Treating Acid Mine Drainage from Abandoned Surface Coal Mines

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***Abstract*- Steel slag leach beds are designed to use a waste product from the steel industry, slag, to add alkalinity to clean water before being mixed with acid mine drainage. In Southern Ohio, steel slag leach beds utilizing slag from electric arc furnaces are a popular method for treating acid mine drainage from abandoned coal mines. In Raccoon Creek Watershed in Ohio, six steel slag leach beds have been constructed in the last year. Three of these, Forest, Meade and Kern Hollow, discharge into the same reach of the East Branch of Raccoon Creek. While the discharge pH of each of these beds averages between 10 and 12, the corresponding alkalinity is not as high as the design assumptions. Additionally, heavy precipitation of calcium carbonate downstream from the steel slag leach bed discharges quickly reduces the alkalinity addition provided by these systems. While the design discharge alkalinity is 1000 mg/L, no alkalinity was measured over 200 mg/L in this study. While steel slag leach beds can be an effective means of treating acid mine drainage, the carbonate concentration of the feed water and the distance between the slag bed discharge and the acidic water will dictate the effectiveness of treatment.**

Keywords- Raccoon Creek; Alkalinity; Passive Treatment

I. INTRODUCTION

Acid mine drainage (AMD) that brings a pervasive environmental problem worldwide is common in the Appalachian Region of the United States where Southern Ohio is located. AMD is produced through the oxidative weathering of pyrite inclusions in coal and the surrounding strata. The coal of Southern Ohio is high in sulphur. There are hundreds of kilometres of streams in Ohio polluted by acid mine drainage. Characteristic chemistry of these streams is low pH, high acidity and high metal concentrations, especially iron, aluminium, and manganese. Due to both the extent of the problem and the limited funds available, passive treatment systems are the preferred method of acid mine drainage treatment.

In the past decade, significant progress has been made towards restoring Ohio streams affected by AMD. Typical AMD treatment systems used include source control, limestone leach beds, lime dosers, limestone channels, wetland systems and steel slag leach beds. Increasingly, steel slag leach beds (SSLBs) are the passive treatment systems of choice because they reuse waste from the steel industry and produce significant alkalinity for AMD treatment. With the uptake of SSLBs come many design complications and challenges to optimize their operation to achieve ecosystem recovery.

Raccoon Creek Watershed in Southern Ohio, shown in Fig. 1, was heavily mined for coal for much of the 20th Century. Throughout the watershed, over 20,000 hectares (50,000 acres) of mines have been abandoned; approximately half were underground workings and half were surface workings. East Branch Subwatershed, in the headwaters of Raccoon Creek, has been one of the most severe sources of acid mine drainage to Raccoon Creek. Three phases of reclamation and remediation have been completed in East Branch for a cost of over $2,000,000. In addition to draining and reclamation of several strip pits, eleven steel slag leach beds have been installed throughout the basin in three phases. Prior to treatment, the Ohio Environmental Protection Agency (OEPA) designated East Branch as “Limited Resource Water”, suggesting that it was unrecoverable. Due to the reliance of the East Branch treatment projects on steel slag, it is an ideal study site for the efficacy of steel slag for AMD treatment.

Fig. 1 Raccoon Creek watershed with East Branch subwatershed highlighted in gray

Steel slag is formed from the addition of calcium compounds to iron ore or scrap during the steelmaking process. To make a stronger and more manageable steel product, limestone, lime, or dolomite is added to remove the aluminium, silicon, and phosphorus ions found in the iron ore. The process results in a slag, which separates to the top of the melt and is disposed of. This glass-like material is a low-cost source of alkalinity suitable for use in the remediation of acid mine drainage [1].

Steel slags consist of calcium alumino-silicate oxides; their composition varies according to the desired quality of steel and the steel-making process involved [1]. Deionized water

passed through one type of basic steel slag yielded metal concentrations within the acceptable limits for a modified U.S. Environmental Protection Agency's Toxicity Characteristic Leaching Procedure (TCLP) and an elevated level of only one metal (Ni) under EPA drinking water standards. Metals present and at acceptable limits included selenium, barium, zinc, lead, beryllium, and chromium [1]. Aluminium, calcium, iron, magnesium, and chlorine were present in other slags [2]. Some slags have been tested with potentially toxic levels of hazardous elements such as fluoride, chromium and vanadium [2] and lead, cadmium, nickel and chromium [3]. A potential disadvantage of the use of SSLBs is the mobilization of metals if the slag's alkalinity is exhausted or an inadequate amount of slag is used. Therefore, it is important to place slag in environments that will not become acidic and to take care when placing slag in non-surface locations [1].

SSLBs are an ideal alternative to limestone in the passive treatment of acid mine damage (AMD) because they have been shown to have a greater daily alkaline load than both open and closed limestone leach beds. In West Virginia, Ziemkiewicz and Skousen [1] measured an alkalinity generation of 1,500 mg/L per day in one open SSLB versus 79 mg/L per day and 196 mg/L per day for open and closed limestone leach beds, respectively. In another study of passive treatment systems in the eastern U.S., the average acid load reduction for slag leech beds was 76 tons/year, compared with 15 tons/year for limestone leach beds and 9 tons/year for open limestone channels, anaerobic wetlands, aerobic wetlands, and vertical flow wetlands [4].

In addition, steel slag can be exposed to CO_2 in the atmosphere without a significant decline in alkalinity production, unlike lime [1], although research in Ohio has found that exposure to atmospheric CO_2 can cause precipitation of calcium carbonate, effectively clogging the beds [5]. Other advantages of SSLBs include a low level of required maintenance, close proximity and high availability of slag to the Appalachian region [1], and relative ease of construction [4]. In addition, reuse of steel slag for the treatment of acidic waters prevents the disposal of the by-product into a landfill as waste, and prevents the extraction of raw limestone from the earth [2].

For the treatment of acid mine drainage, slag with a 1/8 inch fine grade is used. Fresh, metal-free runoff or rainfall should serve as influent for a SSLB system. The alkaline effluent out of the system can treat AMD in-situ or can be allowed to flow into acidic waters downstream from the source of AMD. Slag can also be used as a direct water treatment when deposited in a stream affected by AMD [1]. SSLBs require a residence time of one to three hours [6] and are often designed for four hours of residence time [7]. The average service life of an SSLB is 6.2 years, although it depends on the configuration, residence time and slag composition.

The alkalinity measured in-stream down gradient from the discharge of steel slag leach beds is highly variable and depends on many design considerations. This paper focuses on the aquatic chemistry measured downstream from three steel slag leach beds, installed during the East Branch Phase II project, on both a large scale (several kilometres) and small scale (750 meters or less). The small scale samples reflect the geochemical changes due to the East Branch Phase II slag beds, while the large scale sampling will reflect the geochemical changes caused by the East Branch Phase I, II and III slag beds. The East Branch Phase II beds studied are named Meade, Forest and Kern and their locations are shown in Fig. 2.

Fig. 2 Long term sampling sites in East Branch subwatershed: sites EB550, EB560 and EB570 represent the location of Mead, Kern Hollow and Forest slag beds and site EB190 represents the discharge from the three projects in total

II. METHODS

Field data was measured with a sonde (equipment: Yellow Springs Institute 600 XLM datasonde) and included temperature (degrees Celsius), pH, specific conductivity (μS/cm), and dissolved oxygen (mg/L and percentage). Water flow was measured at each site with either a SonTek FlowTracker Handheld-ADV, a pygmy flow meter, a Marsh-McBirney flow meter, or a Baski collapsible cutthroat flume. The immediate alkalinity gradient downstream from each steel slag leach bed was measured using a Hach digital titrator to both phenolphthalein and methyl red-bromocresol green endpoints. Filtered preserved, non-filtered preserved, and non-filtered non-preserved samples were gathered and sent to the Ohio Department of Natural Resources–Division of Mineral Resources Management Environmental Lab in Cambridge, Ohio for analysis of chemical water quality characteristics. Lab analysis of samples was performed for acidity, alkalinity, pH, temperature, specific conductance, hardness, total dissolved solids, total suspended solids, dissolved oxygen, sulfate, calcium, magnesium, aluminum, iron and manganese using a Perkin Elmer Optima 2000 ICP, a Dionex ICS-2000 Ion Chromatography system and a Brinkmann Automated Titration system.

Sample sites, shown in Fig. 2, were each sampled as part of either long term monitoring or pre and post construction sampling. In addition, in this study, field parameters (pH, TDS, specific conductivity, temperature, Eh and alkalinity) were measured downstream from the discharge of each slag bed. The intention was to sample downstream of the slag beds at 150 m, 300 m, 450 m, 600 m and 750 m downstream from the slag bed discharge. This plan was followed for Kern Hollow slag bed; however, only the first four samples could be taken for Meade, because the small tributary that Meade discharges into is not long enough for the entire sampling protocol. Forest slag bed also had some variation because

approximately 300 m downstream from the slag bed discharge, the stream flows through a small wetland; samples were taken 150 m and 300 m downstream from the slag bed discharge, at the wetland outlet and 150 m, 300 m and 450 m downstream from the wetland outlet.

In addition to the small spatial scale samples taken downstream from each slag beds, three long term monitoring sites were used in this analysis, all are shown in Fig. 2. Site EB190 represents the discharge of all three East Branch Phase II slag beds. Site EB047 is a sample location on the mainstem of East Branch 6.4 kilometers (four miles) downstream from EB190. Site EB010 is a sample location at the mouth of East Branch before it discharges into the mainstem of Raccoon Creek.

III. RESULTS AND DISCUSSION

The aquatic chemistry of East Branch is complex and is influenced not only by the three slag beds examined in this study, but also the East Branch Phase I steel slag leach beds and the East Branch Phase III slag bed that was in construction during some of the data collection and was functioning by the end of this study. As shown in Fig. 3, the net alkalinity of all three sites sampled on the main stem of East Branch (EB190, EB047, EB010) were typically net acidic before there was any treatment in East Branch subwatershed. Some improvement on the main stem is seen in the data presented in Fig. 3 after the first treatment project in the subwatershed was completed.

While it is difficult to tease out the effects of different treatment phases in Fig. 3, Fig. 4 shows the improved net alkalinity at site EB190 post-completion of East Branch Phase II in the six months before construction was complete and the 9 months after construction was completed. While the reclamation and remediation projects completed during East Branch Phase I improved the net alkalinity at EB047 and EB010, the impact of East Branch Phase II treatment projects can only be seen at EB190. At EB190, the pH increased from being consistently below 6 to being consistently between 6 and 7. In Fig. 5, an initial spike in pH can be seen in the first month after construction was completed, but the pH settles to a consistent value quite quickly.

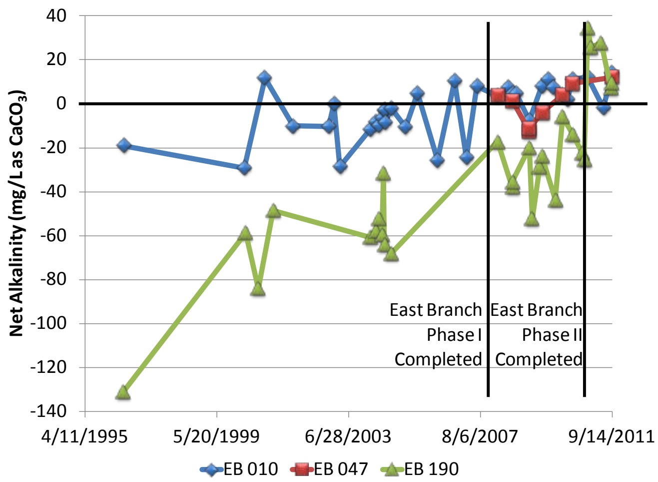

Fig. 3 Net alkalinity at the discharge of East Branch Phase II, EB 190 (Meade, Kern Hollow, and forest slag beds), four miles downstream from the project discharge, EB 047, and the mouth of East Branch, EB 010

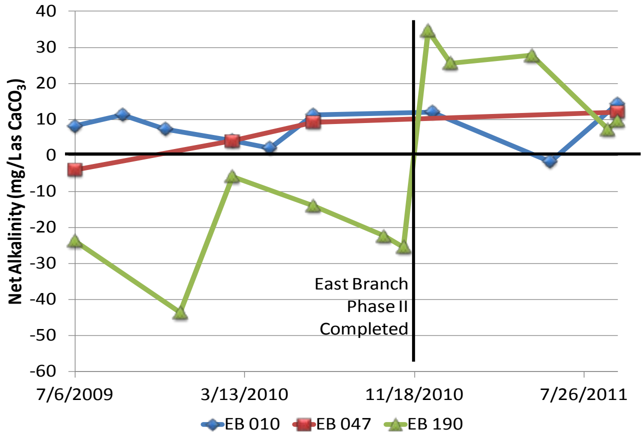

Fig. 4 Net alkalinity downstream from East Branch Phase II project discharge for six months before completion and nine months post completion

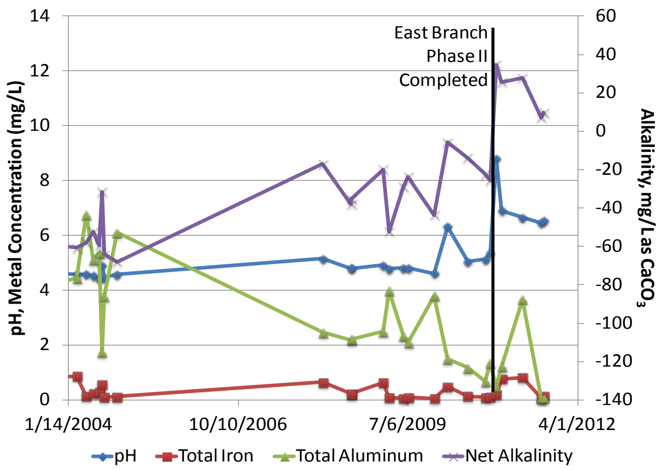

Fig. 5 Aquatic chemistry at EB190, the combined discharge of all three slag beds that are part of the East Branch Phase II project

The impact of multiple projects in a single subwatershed are difficult to isolate from each other, in the case of East Branch Phase II, sample site EB190 is the only long term monitoring site that shows significant changes in aquatic chemistry after construction of East Branch Phase II slag beds. Fig. 5 shows the increased pH and net alkalinity at EB190 after construction. Additionally, Fig. 5 shows the variability in both total iron and total aluminum due to instream precipitation of metals. If metal capture was incorporated into the treatment system, a reduction in total metals may have been seen at EB190.

The discharge from each steel slag leach bed is highly alkaline when compared to the source water (Fig. 6). This would suggest that the receiving waters from each steel slag bed would also have net alkalinity far in excess of the source waters for some distance downstream. Closer examination, as shown in Fig. 7, shows that although the pH of each receiving stream is elevated compared to their pre-treatment levels of 3.5–4.5, they are several points lower than those seen in the discharges of the steel slag beds (varying from 11.3–12.5 since construction). Additionally, the alkalinity in the receiving streams is over one order of magnitude lower than that of the slag bed discharge within 150 meters downstream. Since this is accompanied by an order of magnitude decrease in total calcium (from about 1000 mg/L to about 100 mg/L), it is likely that the alkalinity is being consumed both by acidic

water, but also by precipitation of calcium carbonate between the slag bed discharge and the receiving stream.

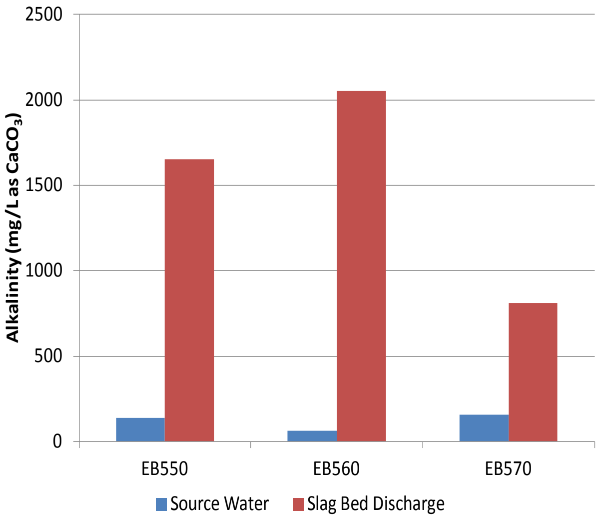

Fig. 6 Net alkalinity of source water and slag bed discharge from each of East Branch Phase II steel slag leach beds

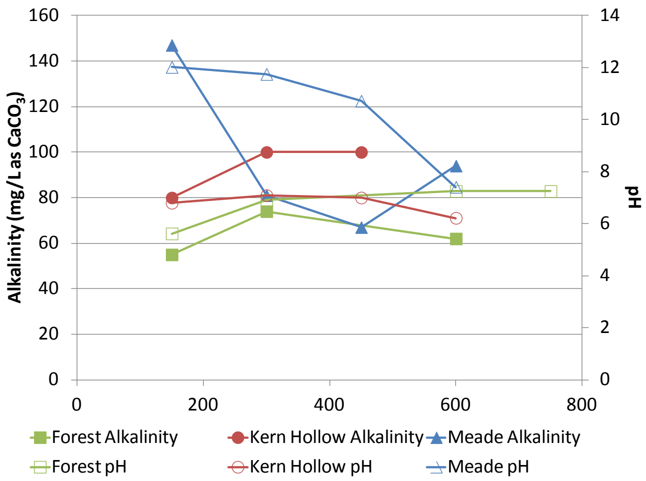

Fig. 7 pH and alkalinity (mg/L as CaCO3) downstream from Forest, Kern Hollow and Meade steel slag leach beds

This is a major shortcoming in the operations of SSLBs and is a hurdle that future designs should be ready to overcome. The geochemistry of SSLBs is complex, but any efforts to reduce the formation of carbonate precipitates will improve their ultimate production of alkalinity within receiving streams. Some possible solutions include installing artificial riffles for excess CO_2 to offgas from the source water.

Since many slag beds have been built in Ohio in the past decade, a great deal of attention has been focused on improving the designs. One of the major issues has been keeping the alkalinity in the water between the slag bed discharge and the receiving stream [7]. Several slag beds have obvious calcium carbonate precipitates in the channel directing water into the stream. More recently, including East Branch Phase II projects, designs have incorporated piping to direct the highly alkaline water closer to the receiving stream. However this data suggest that the alkalinity does not persist far downstream from the slag bed discharge. Despite this, the aquatic chemistry at EB190 has shown improvement and the three phases of East Branch reclamation and remediation are beginning to bring life back to the East Branch of Raccoon Creek.

IV. CONCLUSIONS

With an increase in use of steel slag leach beds for acid mine drainage treatment, it is necessary to determine what distance of stream is necessary downstream of a slag bed before biological recovery occurs. This analysis suggests that this assessment should be done at two spatial scales, within 1000 meters of the slag bed discharge and within several kilometers of the slag bed discharge. The evolution of alkalinity production from steel slag leach beds both temporally and spatially is a great predictor for both slag bed failure and stream recovery.

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REFERENCES

[1] P.F. Ziemkiewicz and J.G. Skousen, "The use of steel slag in mine drainage treatment and control," In: *Proceedings, 19th Annual West Virginia Surface Mine Drainage Task Force Symposium*, Morganttown, West Virginia, April 1998.

[2] C.S. Gahan, M.L. Cunha, and A. Sandstrom, "Comparative study on different steel slags as neutralizing agent in bioleaching," *Hydrometallurgy*, vol 95, pp. 190-197, 2009.

[3] M.S. El-Mahllawy, "Characteristics of acid resisting bricks made from quarry residues and waste steel slag," *Construction and Building Materials*, vol. 22, pp. 1889-1896, 2007.

[4] J.G. Skousen and P. Ziemkiewicz, "Performance of 116 passive treatment systems for acid mine drainage. *American Society of Mining and Reclamation*, 2005.

[5] R.G. Reifler and E. Goetz, "Remediation of Acid Mine Drainage: Performance of Steel Slag Leach Beds," In: *Proceedings of National Association of Abandoned Mine Land Programs*, Scranton, Pennsylvania, September 2010.

[6] J. Simmons, P. Ziemkiewicz, and D.C. Black, "Use of steel slag leach beds for the treatment of acid mine drainage: The McCarty Highwall Project," *American Society of Mining and Reclamation*, 2002.

[7] M. Farley, Personal Communication, 2009.

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